

Claims

R2 WHAT IS CLAIMED IS:

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- 5 1. A chromium(VI)-free, chromium(III)-containing and substantially coherent conversion layer on zinc or zinc alloys, characterised in that
- 10 even in the absence of further components such as silicate, cerium, aluminum and borate it presents a corrosion protection of approx. 100 to 1000 h in the salt spray test according to DIN 50021 SS or ASTM B 117-73 until first attack according to DIN 50961 Chapter 10;
- 15 it is clear, transparent and essentially colorless and presents multi-colored iridescence;
- 20 it has a layer thickness of approx. 100 nm to 1000 nm; and
- it is hard, adheres well and is resistant to wiping.
- 25 2. A conversion layer according to claim 1, characterised in that it has across the conversion layer thickness a chromium content of up to approx. 1%, in relation to zinc and chromium in the conversion layer an average chromium content of more than approx. 5%;
- 30 it has a chromium-rich zone > approx. 20% chromium, in relation to zinc and chromium in the conversion layer, of more than approx. 15 nm; and
- it has a chromium index > approx. 10.

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3. A conversion layer according to claim 1 or 2, characterised in that it may contain, for further enhanced corrosion protection,

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additional components selected from the group consisting of:  
silicate, cerium, aluminum and borate;

additional metal compounds, in particular 1- to 6-valent metal  
compounds, for example compounds of Na, Ag, Al, Co, Ni, Fe,  
Ga, In, lanthanides, Zr, Sc, Ti, V, Cr, Mn, Cu, Zn, Y, Nb, Mo,  
Hf, Ta, W; and

anions, in particular halide ions, in particular chloride ions;  
sulfurous ions, in particular sulfate ions, nitrate ions;  
phosphoric ions, in particular phosphate ions, diphosphate  
ions, linear and/or cyclic oligophosphate ions, linear and/or  
cyclic polyphosphate ions, hydrogen phosphate ions;  
carboxylic acid anions; and silicon-containing anions, in  
particular silicate anions; and

polymers, in particular organic polymers, corrosion inhibitors;  
silicic acids, in particular colloidal or disperse silicic acids;  
surfactants; diols, triols, polyols; organic acids, in particular  
monocarboxylic acids; amines; plastics dispersions; dyes,  
pigments, in particular carbon black, chromogenic agents, in  
particular metallic chromogenic agents; amino acids, in  
particular glycin; siccatives, in particular cobalt siccatives;  
dispersing agents; and

mixtures thereof.

4. A conversion layer according to any one of claims 1 to 3,  
characterised in that it is a basis for further inorganic and/or  
organic layers.
5. A conversion layer according to any one of claims 1 to 4,  
characterised in that it contains dyes or color pigments for  
modification of the inherent color thereof.
6. A conversion layer according to any one of claims 1 to 5,  
characterised in that its layer thickness is approx. 100 nm.

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7 A method for producing chromium(VI)-free conversion layers affording at least the corrosion protection of conventional chromium(VI)-containing yellow chromations, wherein

a metallic surface, in particular one of zinc or zinc alloys, in particular with iron, is treated with a solution of at least one chromium(III) complex and at least one salt;

10 **characterised in that**

the concentration of the chromium(III) complex is increased in comparison with a conventional trivalent blue chromation; and/or

15 a chromium(III) complex is used having ligand replacement kinetics more rapid than the fluoride replacement kinetics in chromium(III)-fluorocomplexes.

20 8. A method according to claim 7, characterised in that treatment is carried out at an elevated temperature, in particular 20 to 100°C, preferably 20 to 80°C, in a preferred manner 30 to 60°C, in a particularly preferred manner 40 to 60°C.

25 Sub H4 9. A method according to any one of claims 7 or 8, characterised in that the ligands of the chromium(III) complex are selected from the group consisting of:

30 chelate ligands, such as dicarboxylic acids, tricarboxylic acids, hydroxycarboxylic acids, in particular oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic acid; and

35 furthermore, maleic acid, phthalic acid, terephthalic acid, tartaric acid, citric acid, malic acid, ascorbic acid; and

further chelate ligands such as acetylacetone, urea, urea derivatives, and

further complex ligands wherein the complexing functional group contains nitrogen, phosphorus or sulfur ( $-NR_2$ ,  $-PR_2$ , wherein R independently is an organic, in particular aliphatic radical and/or H, and/or  $-SR$ , wherein R is an organic, in particular aliphatic radical or H); phosphinates and phosphinate derivatives; as well as

suitable mixtures thereof, among each other as well as in mixed complexes with inorganic anions and  $H_2O$  and/or

the method is performed repeatedly on the surface to be passivated.

10. A concentrate for producing a passivation solution for surfaces of zinc or zinc alloys, in particular ones with iron, wherein it substantially contains chromium(III) for a passivating component,

characterised in that

the chromium(III) is present in the form of at least one complex having ligand replacement kinetics more rapid than the fluoride replacement kinetics in chromium(III)-fluorocomplexes.

11. A concentrate according to claim 10, characterised in that the chromium(III) complex is selected from complexes with chromium(III) and at least one ligand from the group consisting of:

chelate ligands, such as dicarboxylic acids, tricarboxylic acids, hydroxycarboxylic acids, in particular oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic acid; and

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and

~~further chelate ligands such as acetylacetone, urea, urea derivatives, and~~

further complex ligands wherein the complexing functional group contains nitrogen, phosphorus or sulfur (-NR<sub>2</sub>, -PR<sub>2</sub>, wherein R independently is an organic, in particular aliphatic radical and/or H, and/or -SR, wherein R is an organic, in particular aliphatic radical or H,); phosphinates and phosphinate derivatives; as well as

suitable mixtures thereof, among each other as well as in mixed complexes with inorganic anions and  $H_2O$ .

12. A concentrate according to any one of claims 10 or 11, characterised in that the concentrate is present in solid or liquid form.

13. A concentrate according to any one of claims 10 to 12, characterised in that it contains further additives selected from the group consisting of: sealers, dewatering fluids; and

additional metal compounds, in particular 1- to 6-valent metal compounds, for example compounds of Na, Ag, Al, Co, Ni, Fe, Ga, In, lanthanides, Zr, Sc, Ti, V, Cr, Mn, Cu, Zn, Y, Nb, Mo, Hf, Ta, W; and

anions, in particular halide ions, in particular chloride ions; sulfurous ions, in particular sulfate ions, nitrate ions; phosphoric ions, in particular phosphate ions, diphosphate ions, linear and/or cyclic oligophosphate ions, linear and/or cyclic polyphosphate ions, hydrogen phosphate ions; carboxylic acid anions; and silicon-containing anions, in particular silicate anions; and

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17. A passivation bath according to any one of claims 14 to 16, characterised in that it contains approx. 20 g/l chromium(III) and has a pH of approx. 2 to 2.5.

18. A passivation bath according to any one of claims 14 to 17, characterised in that it contains further additives in particular selected from the group consisting of sealers, dewatering fluids; and

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additional metal compounds, in particular 1- to 6-valent metal compounds, for example compounds of Na, Ag, Al, Co, Ni, Fe, Ga, In, lanthanides, Zr, Sc, Ti, V, Cr, Mn, Cu, Zn, Y, Nb, Mo, Hf, Ta, W; and

anions, in particular halide ions, in particular chloride ions; sulfurous ions, in particular sulfate ions, nitrate ions; phosphoric ions, in particular phosphate ions, diphosphate ions, linear and/or cyclic oligophosphate ions, linear and/or cyclic polyphosphate ions, hydrogen phosphate ions; carboxylic acid anions; and silicon-containing anions, in particular silicate anions; and

polymers, corrosion inhibitors; silicic acids, in particular colloidal or disperse silicic acids; surfactants; diols, triols, polyols; organic acids, in particular monocarboxylic acids; amines; plastics dispersions; dyes, pigments, in particular carbon black, chromogenic agents, in particular metallic chromogenic agents; amino acids, in particular glycine; siccatives, in particular cobalt siccative; dispersing agents; as well as

mixtures thereof.

19. A passivation bath according to any one of claims 14 to 18, characterised in that it has a bath temperature of approx. 20 to 100°C, preferably 20 to 80°C, in a preferred manner 30 to 60°C, in a particularly preferred manner 40 to 60°C.

20. A method for passivating surfaces of zinc or zinc alloys, in particular ones with iron,

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